

A Fast-GC/MS System to Measure C₂ to C₅ Carbonyls, Methanol and Ethanol Aboard Aircraft

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Abstract

A fast response gas chromatograph/mass spectrometer (FGCMS) instrument to measure $\leq C_5$ carbonyl compounds, methanol and ethanol was developed for the NASA GTE TRACE-P (Global Tropospheric Experiment, Transport And Chemical Evolution Over The Pacific) mission. The system consists of 4 major components: sample inlet, preconcentration system, gas chromatograph (GC), and detector. The preconcentration system is a custom-built cryogen-conservative system. The GC is a compact, custom-built unit that can be temperature programmed and rapidly cooled. Detection is accomplished with an Agilent Technologies 5973 mass spectrometer. The FGCMS instrument provides unambiguous identification because the compounds are chromatographically separated and mass selected. During TRACE-P, a sample was analyzed every 5 minutes. The FGCMS sensitivity was between 5 and 50 pptv, depending on the compound. The instrument package consumes less than 2000 watts and is fully automated with LabVIEW™ 6i. Methods were developed for producing highly accurate gas phase standards for the target compounds and for testing the system in the presence of potential interferents. This paper presents data on these tests and on the general overall performance of the system in the laboratory and also aboard the DC-8 aircraft during the mission. Achievable substantial enhancements of the instrument capability in terms of time resolution and compound coverage are discussed.

I. Introduction

Oxygenated volatile organic compounds (OVOCs) are important constituents of the troposphere because of their role in key oxidation cycles. Currently, information on atmospheric distributions of these compounds is limited because only recently have ground-based measurements become common and relatively few measurements have been recorded on aircraft platforms. More complete data on the distribution, sources, and sinks of this compound class will ultimately lead to a better understanding of atmospheric chemistry through better models that explicitly take into account contributions of these species to the photooxidation mechanisms at work in the troposphere.

A number of methods have been used for quantifying ambient OVOC mixing ratios. The intent here is not to give a comprehensive review of measurement techniques but to briefly overview the subject matter that pertains to this paper. An early but still relevant review on the subject of carbonyl measurements may be found in Vairavamurthy et al., [1992]. At that time, there were a number of competing techniques, ranging from liquid scrubbing chemical derivatization followed by liquid chromatography to spectroscopic methods. None of the techniques had distinguished themselves as reliable techniques for ambient carbonyl determination despite nearly a decade of analytical development. The DNPH (2,4-dinitrophenylhydrazine) cartridge technique has been used extensively during the last decade for ambient measurements of formaldehyde and higher carbonyls. This method was adopted by the United States Environmental Protection Agency (USEPA) for measuring formaldehyde, acetaldehyde and acetone throughout the PAMS (Photochemical Assessment Monitoring Stations) network. PAMS was instituted following the 1990 Clean Air Act Amendments (CAAA). The CAAA required States to establish sites to monitor ozone, oxides of nitrogen

(NO_x), and volatile organic compounds (VOCs) in order obtain more comprehensive and representative data on ozone air pollution in affected areas. Drawbacks to the technique have been documented in the literature [Vairavamurthy et al., 1992, Sirju and Shepson, 1995, Apel et al., 1998] and include high blanks, ozone interference, and the requirement for long sampling times (tens of minutes to hours) to achieve high pptv to low ppbv detection limits.

Gas chromatography has also been used, most commonly in ground-based applications, to measure a number of OVOCs including alcohols, aldehydes (> C₁) and ketones. For a recent compilation of GC techniques used to measure VOCs in ambient air, please see Helmig et al., [1999]. The most commonly used detectors for GC OVOC measurements have been the flame ionization detector (FID) and mass spectrometry (MS). Since the FID detector is nonspecific it is imperative that good peak separation through good chromatography is accomplished to minimize the potential for co-elutions of target and non-target VOCs. Excellent examples of this technique can be found in Schade et al., [2000] and Goldan et al., [1995]. GC-MS has become an increasingly popular technique for ground-based studies of OVOCs [e.g., Helmig et al., 1994, Yokouchi et al., 1994, Montzka et al., 1993, 1995, Liebrock and Slemr, 1997, Biesenthal et al., 1997, Starn et al., 1998, Riemer et al., 1998, and Apel et al., 2002]. High sensitivity and excellent selectivity are characteristic of modern GC-MS systems. Other techniques that have been developed and deployed include GC/Atomic Emission Detection (GC/AED) [Apel et al., 1998 and Greenberg et al., 1999] and GC/Reduction Gas Detector (GC/RGD) [O'Hara and Singh, 1988].

Airborne atmospheric chemistry experimental platforms have become more sophisticated in recent years [<http://www-gte.larc.nasa.gov>, <http://topse.acd.ucar.edu/>]. These platforms are capable of high spatial coverage over an abbreviated time period. Important information on

distributions of key atmospheric species can be gained in a single campaign. Requirements for aircraft-based measurements are more stringent than for ground-based measurements. The highest possible temporal resolution and sensitivities are desired. A number of techniques have been developed to measure OVOCs aboard aircraft. Chemical Ionization Mass Spectrometry (CIMS) techniques have been deployed on a number of missions to measure OVOCs in the troposphere [Arnold et al., 1986, 1997, Möhler et al., 1993, Wohlfrom et al., 1999, Warneke et al. 2001, Sprung et al., 2001, Wisthaler et al., 2001]. These techniques are characterized by relatively good sensitivities (tens of pptv) and good time resolution (seconds to 1 minute). Selectivity is a concern with the CIMS techniques since the ion (or ions) being monitored for quantification may not be specific only to the compound (or compounds) of interest. The GC/RGD technique has been used by Singh et al. [1994, 1995, 2000, this study] to measure acetone and other OVOCs in the upper troposphere. The RGD detector has been shown to be about a factor of ten times more sensitive than the FID for carbonyls [O'Hara and Singh, 1988] and is also more selective. Although proven to be a viable technique by Singh et al. [1995], less than optimal chromatography appears to be a characteristic feature and strict attention to operational details is necessary for quantitative and reproducible results. Recently, an FTIR spectrometer has been deployed to study biomass-burning plumes [Yokelson et al., 1999]. An advantage of this system is that many compounds can be observed simultaneously with high temporal resolution. A drawback is that the sensitivity is lower than some of the other techniques.

In implementing any of the techniques described above, experimentalists must be aware of the potential for artifact formation either in the inlet or in the analytical system itself and of difficulties in efficient transfer of these polar compounds through the inlet and into the analytical

system. Artifact formation when sampling carbonyl compounds is discussed in Vairavamurthy et al., [1992]; ozone, sulfur dioxide, and nitrogen dioxide are listed as potential interfering compounds. Others have mentioned artifact formation [Goldan et al., 1995; Riemer et al., 1998], however most have neglected to conduct the necessary tests.

There have been few instrument comparisons of carbonyl measurement techniques and none that we are aware of for alcohols. Apel et al. [1998] have recently reported on a ground-based comparison of GC-MS instruments with cartridge-based techniques for the measurement of carbonyl compounds. Differences of a factor of two in the data were common and it was noted that a more formal intercomparison of techniques would be desirable. More recently a CIMS technique and a GC based technique simultaneously measured acetone aboard an aircraft over the North Atlantic free-troposphere and lower stratosphere [Wohlfrum et al., 1999]. In this latter experiment the acetone data obtained by both instruments in the same air masses agree to within approximately 50%.

For TRACE-P, we developed and deployed the first airborne GC/MS system for OVOC measurements. This technique has a number of advantages over others. It is as sensitive as the RGD detector but is more selective and is capable of measuring a number of different compound classes in addition to OVOCs, including halocarbons and non-methane hydrocarbons (NMHCs). In this paper, a description is given of the design and operation of this aircraft technique. Data is presented to demonstrate the feasibility of this method.

Experiment

The GC/MS method reported here is similar in basic operating principle to ground-based techniques that investigators have developed. The differences are that a more sophisticated inlet

is needed for aircraft sampling; the cryogenic preconcentrator must be extremely efficient to allow rapid sample enrichment and must also be conservative in its consumption of cryogen because of the limited cryogen available on aircraft; the gas chromatograph must be miniaturized; the system must be able to withstand significant vibrations and G-forces; the zero/calibration system must provide periodic calibration and zeros for the inlet while maintaining ambient humidity; the system must be fully automated, and the response time must be rapid. The various components of the system will be described in subsections below.

1. Inlet and sampling system

A schematic of the inlet and sampling system is shown in Figure 1. The inlet consisted of 2 ports extending approximately 35 cm orthogonal from a window plate of the DC-8 aircraft through a designed aerodynamic housing. The inlet length was determined by the requirement to sample beyond the boundary layer of the aircraft. The forward port (port 1) served as the inlet to the FGCMS system. It consisted of an electropolished stainless steel (ss) tube extending 0.75 cm beyond the housing into the ambient atmosphere. A temperature-controlled (50 °C) copper block encased the ss tube near the tip of the inlet. Within the housing the inlet tube was coupled to a heated 0.635 cm O.D. SiloniteTM fused silica lined ss tubing that extended to the FGCMS. The aft port (port 2) was the inlet for the zero air/calibration system that will be described later. The inlet tip was a machined piece of aluminum (0.5 cm O.D.) extending 1.25 cm from the housing into the ambient atmosphere. A non-heated 0.635 cm O.D. TeflonTM tube connected the inlet tip to the zero air generator/calibration (ZA/CS) system.

The inlet was designed so that three functions could be performed: zeroing, calibrations, and ambient air sampling. Zeroing of the inlet was performed by scrubbing ambient air taken in from

port 2 with the on-board zero air generator and returning the scrubbed air towards the front of port 1 and overfilling the inlet, i.e., providing 20% - 50% more flow of scrubbed air than air taken in to the FGCMS from port 1. Calibrations were performed in much the same way with the only difference being that a metered flow of calibration standard was introduced into a known flow rate of the scrubbed air prior to returning the scrubbed air to the inlet. For ambient air sampling, the valve leading to the ZA/CS was shut off and ambient air was taken, by way of a Teflon diaphragm pump (KNF Neuberger Model NO35STI), into the FGCMS analytical system.

2. Cryogenic Preconcentrator

A number of different approaches have been used to preconcentrate VOC compounds for GC analysis. Helmig et al., [1999], gives a summary listing. Rapid sample cycles and the desire for artifact-free analyses were driving forces behind choosing a fully cryogenic concentrator for this work. An additional requirement for aircraft-based systems is low liquid nitrogen (LN₂) consumption. With these prerequisites and no commercial or research technology that met our design criteria, a novel preconcentration system was designed and subsequently built.

Key components of the preconcentrator are shown in Figure 2. It consists of a custom-built 10 liter dewar (Cryofab, MA) that has three coils situated near the bottom. Each coil provides cooling to one of three traps, the water trap, the enrichment trap, and the cryofocuser. Nitrogen gas from the LN₂ dewar headspace enters the coils that are immersed in liquid nitrogen. Flowing the cooled nitrogen gas through the heat exchange coils, which are directly connected to the traps, provides rapid cooling for each of the three traps. Temperatures are measured with thermocouples which serve as inputs to a WatlowTM CLS 216 temperature controller described in section 6. The Watlow servoed the mass flow controllers, through an external digital to analog

converter, to control the trap temperatures. The total liquid nitrogen consumption rate is approximately 0.5 liters hr^{-1} .

3. Gas Chromatograph

Figure 3 shows a visual representation (SolidWorksTM) of the gas chromatograph that was used in this study. The dimensions of the unit are 18 cm x 18 cm x 10 cm. The body of the GC oven is constructed of machined MariniteTM M insulator material. Inside the oven a ss mandrel serves as a support for the GC column and for a flexible heater element situated on the opposite side of the column. The faceplates are made out of stainless steel with cut channels to allow for airflow through the oven body. On each face is mounted a ss shutter that has matching open channels (with faceplates) when in the open position and closes the oven when in the closed position. The GC oven temperature programming occurs in the closed position. All temperatures including the oven temperature are controlled through a Watlow CLS-216 capable of controlling up to 16 separate temperature zones (see Section 6). To return to the starting point temperature in preparation for the next GC run, the heater is shut off, a solenoid fires to open the shutter and a fan (55 cubic feet per minute) is turned on.

4. Detector

The FGCMS uses a modified Agilent Technologies 5973N quadrupole mass spectrometer system. Agilent equips the system with an Edwards EXT 250 turbomolecular pump that has a pumping capacity of 220 L s^{-1} He maximum displacement. Because of metallic bearings, the pump is only rated for 1 G (gravity force). Therefore, this pump was replaced by a Varian Model V301 NAV (220 L s^{-1} He maximum displacement) turbomolecular pump with all ceramic

bearings, rated to 3 G's. This change required the addition of a Varian turbo pump controller and also required the modification of the pump control electronics of the 5973N. The mass spectrometer was operated in the electron ionization single ion mode throughout the study. A laptop personal computer running HPChemstationTM software controlled the system.

5. Zero air/ Calibration System (ZA/CS)

Establishing good zeros and obtaining accurate calibrations is at the heart of quantitative measurements. We tested a number of commercially produced ultra high purity zero air generation systems, hydrocarbon-free cylinder air, and cylinder N₂ sources and found that for the TRACE-P work, the trace levels of carbonyls in the cylinders were variable and often at unacceptable levels. We have also found that transmission of OVOCs through sampling lines is facilitated greatly by having humidity in the gas stream. A solution to these problems was to build a catalytic zero air generator that scrubs OVOCs to limit of detection values while maintaining ambient humidity levels. Figure 4 shows a schema of our system. Ambient air is drawn through a 2 µm ss filter (Swagelok[®], SS-4FW-2) into the ZA/CS through a KNF Neuberger Teflon diaphragm pump (UN828ANDC). After exiting the pump, the air passes through a "T" fitting that houses a poppet valve set to 3 pounds per square inch (PSIG). This allows the pump to operate at full, unrestricted, flow while the ZA/CS may be operating at low flow. The air then passes through a 0.50 L stainless ballast volume which dampens pressure fluctuations due to the pump. Air flow is controlled (0-10 slpm) with an electronic mass flow controller (Tylan, FC-280S) prior to entering the catalyst tube. The scrubbed air is then passed through another filter, into a cooling coil, and then to the outlet.

Figure 5 shows the results of scrubbing a sample containing VOCs at the 3-10 ppb level. The top panel shows the analysis when the sample is taken directly into the analytical system without scrubbing. The bottom panel shows the result of passing the identical gas stream through the catalytic converter operating at 5 liters per minute and 425 °C. All VOC compounds are scrubbed to below limit of detection values (< 5 pptv). The system deployed during TRACE-P had less scrubbing capacity than the present system described here and could only run optimally at less than 4 slm^{-1} . During deployment, zeroing of the system was accomplished by scrubbing ambient air, returning the VOC-free air to the sample inlet (Figure 1), and overflowing the inlet so that only the scrubbed air was sampled.

The system was also configured as a dynamic dilution device. OVOC standards were introduced into a mass flow controller (0–10 sccm or 0-100 sccm). The system was capable of diluting standard mixtures by factors of 10 to 10,000 and it was very accurate because only two calibrated flow controllers were used, the mass flow control of the standard and a 0-10 slpmflow controller for the scrubbed air diluent gas. As with the zero air, the diluted standard samples followed a path identical to the ambient air samples through the analytical system.

Standards for this study were gravimetrically prepared in aluminum cylinders at NCAR. Table 1 shows the mixing ratios of the standard (NASA A) used during TRACE-P. Standards were analyzed multiple times in the laboratory before and after the experiment. Mixing ratios for the standards were determined by the gravimetric value and were checked against a number of other standards prepared both by our laboratory and other laboratories. All compounds showed good stability ($\pm 5\%$) except for acetaldehyde which decreased by $\sim 9\%$ and pentanal and pentanone which decreased by more than 30% from the time of preparation until the post-experiment

analysis (6 months). Because of very low observed mixing ratios and instability in the cylinders, pentanal and pentanone were not reported in the final data submission.

Independent methods of standards generation and analysis that agree increase the confidence in the overall accuracy of the standards. We constructed a 6-position device for standards generation based upon permeation tubes and employing gravimetry as the method of calibration. We have permeation tubes for methanol, acetaldehyde, propanal, acetone, methyl ethyl ketone, and toluene. This system consists of six independent aluminum ovens, each housing one permeation tube. The ovens are temperature controlled to within ± 0.1 °C. The tubes are contained in glass housings with high purity nitrogen continuously flowing over them. A dynamic dilution system has been constructed to control, mix and dilute the permeation tube effluent to the ppmv to pptv concentration levels. Although the tubes are factory calibrated we are also characterizing them using a Mettler balance capable of measuring to ± 10 µg.

The top panel in Figure 6 shows our analysis of the 6 tubes at once (however, note that for quantification our normal procedure is to run each permeation tube separately using a highly characterized diluent flow rate). The bottom panel shows our analysis by GC-FID of a high-pressure cylinder that was prepared containing acetaldehyde, methanol, ethanol, propanal, acetone, butanal and methyl ethyl ketone. Note that all compound peaks are well resolved and easily quantified. Together with the GC-FID analysis, an independent spectroscopic (FTIR) method was used to ascertain the concentrations of compounds gravimetrically prepared in a high-pressure cylinder at 3.0 ppmv. Table 2 shows the results of the comparison of the high-pressure cylinder preparation results with the permeation tubes and the FTIR analysis. Good comparability is observed for the cylinder preparation and the permeation tubes for methanol and acetone. We do not have reliable permeation tube values for acetaldehyde and propanal; although the initial

values we obtained were close to the manufacturer's certified rate, their permeation rates increased over time. This occurred despite the fact that we used N₂ sweep gas and maintained the permeation tubes at 30 °C. The manufacturer (VICI, Houston, TX) is aware that there is a problem with the aldehyde permeation tubes and is working with us to help resolve it. Difficulty in using and preparing permeation tubes for acetaldehyde and other aldehydes has been noted by others [Singh et al., 1995, Riemer et al .1998]. No permeation tube values are reported for MEK because at the time of the experiment we had only recently put this tube into our system and hence did not have it long enough to obtain an accurate weight loss over time.

The FTIR values agree within the error of the measurement with the gravimetric cylinder values for all compounds measured except for MEK. The reasons for this are unclear and are being investigated further. The well-characterized 3 ppmv cylinder was checked against the NASA A cylinder (Table 1) via GC-FID; all compounds agreed to $\pm 5\%$.

To help ensure the accuracy of our in-flight alcohol and carbonyl measurements we also analyzed carbon tetrachloride, a species that is stable and present at a nearly constant mixing ratio in the troposphere, as part of each chromatographic run during the TRACE-P experiment. This allowed us to account for small variations in mass spectrometer response.

6. Data Acquisition and Automated Control of Instrument

The FGCMS instrument operation was controlled with a PCI bus desktop computer running a graphical user interface (GUI) written in National Instruments (NI) LabVIEW™ 6i coupled to two PCI bus data acquisition/control cards and a Watlow temperature controller. The cards (NI PXI-6025E) provided 16 channels of 12 bit differential input A/D, 4 channels of 12 bit D/A analog output and 64 digital I/O lines. The temperature controller provided readout and control

of 16 temperature channels. The Watlow controller (CLS200 16 channel) was operated from within LabVIEW™ via a third party software package (Anaview, SEG Software) and connected to the system via a serial port.

The main LabVIEW™ code and five subroutines were structured so A/D, D/A, digital I/O and serial communications were queried/controlled once per second. Each A/D channel was measured 10 times at 1 kHz. The values were then averaged to 1 second means and scaled to proper engineering units. Nine gas flows, 15 temperatures, 13 logic states, and 14 serial stream data channels from the NASA DC-8, constituted 51 parameters which were displayed on the GUI and written at 5 second intervals into an ASCII text file.

The GUI (Figure 7) is arranged into logical blocks. Setpoints and measured values of flows and temperatures are in the lower left and lower right, respectively. Temperatures and flows could be altered during operation directly on these panels. Logical (Boolean) states for valve positions are displayed in the lower center region. The code performed the intricate time sequencing necessary for sample acquisition, water removal, pre-concentration, cryofocusing, GC injection and oven temperature programming. The timing for each of these steps was adjustable on-the-fly in the upper left region of the GUI. The status of the GCMS sequencing at any moment is shown with the logical state display in the center section of the GUI, beginning with “load sample” and progressing to “cooldown GC”. A graphical display of the GC oven temperature is shown in the top center of the GUI.

A serial data stream available on the DC-8 could be monitored for various state parameters of the aircraft and chemical sensor feeds. Some of this data block is shown in the upper right. LN₂ level, instrumental mode and other instrument and data acquisition control parameters reside in the upper portion of the GUI. Output files were automatically generated according to date/time

of execution and are shown in the upper left corner of the GUI. Just below the file name is a box where experimentalist comments could be entered and placed, in real time, into the output file.

7. FGCMS Instrument layout

Figure 8 shows a photograph of the FGCMS instrument. A number of the individual components that are visible from this view are labeled: (1) the ZA/CS, (2) the pumping station, (3) the gas standard and He carrier gas station, (4) the HP5973N mass spectrometer, (5) dewar/preconcentration system, (6) the computer used for system automation, and (7) the box containing the control electronics.

A. Operation of the FGCMS Instrument

Please refer to Figure 1 for this discussion. Ambient air was drawn from the inlet (port 1) to the analytical system. During TRACE-P a KNF Neuberger Teflon diaphragm pump (UN-035STI) was used but has since been replaced with a metal bellows pump (Senior Aerospace, MB-602). The air sample continuously flowed through the inlet and through the 1-liter SiloniteTM-coated ss holding volume maintained at 760 torr with an MKS Model 640A backpressure regulator. An analytical run was started by switching valve 1, thereby closing off the 1-liter holding volume. Sample was then drawn off the holding volume at a rate of 75 sccm for 80 seconds, yielding a total air sample of 100 cm³. The sample was passed through the first stage trap, an 8 cm x 0.3175 cm PFA teflon tube maintained at -20 °C which was designed to remove water from the sample. It was then passed into the enrichment trap that consisted of a 7.5 cm x 0.3175 cm o.d. Silico steel tube filled with silanized glass wool and maintained near -110 °C. It was here that the compounds of interest were initially trapped. Valve 2 was switched, the

enrichment trap was heated and helium carrier gas swept the compounds of interest to the cryofocusing trap, a 7.5 cm piece of 0.080 cm silicosteelTM tubing maintained at $-120\text{ }^{\circ}\text{C}$. The cryofocusing trap was then rapidly heated, transferring the compounds of interest to the head of a 10 m, 0.18 mm i.d., 1.4 μm phase thickness DB-624 column. The GC oven was held initially at $35\text{ }^{\circ}\text{C}$ for 30 seconds and temperature programmed at a rate of $25\text{ }^{\circ}\text{C}/\text{min}$ until the oven reached $110\text{ }^{\circ}\text{C}$ giving a total run time of 3.5 minutes. The carrier gas flowrate was maintained at 4 sccm using a Tylan FC-280 Mass Flow Controller. The oven cooling time was 1.5 minutes.

B. Calibration and Instrument Testing

A 2 meter all-glass manifold was assembled to provide known quantities of VOC and potential interferent species for calibration and testing the FGCMS (Figure 9). Because the instrument was not completed until the second test flight, this testing took place at NCAR after the TRACE-P mission; under normal circumstances the testing would occur prior to the mission. Laboratory air was first scrubbed free of VOCs, water, and other trace gases and calibrated amounts of the species of interest were then added. An AADCO Model 737-12 provided up to 30 slpm ultra pure air with less than 1 ppm water and ambient levels of CO_2 . Calibrated levels of O_3 , SO_2 , H_2O and NO/NO_2 could be added to the pure air stream through designated ports on the manifold. Detection techniques, described by Gilpin et al.[1997], were used to continuously monitor the levels of these calibrated trace gas levels within the air stream.

Figure 10 shows an example of the calibration curves that we obtained for the compounds measured during the TRACE-P mission. The curves are shown to be linear and also give an indication of detection limits. Detection limits, determined as five times the baseline noise, are given in Table 3. The ethanol measurement was partially compromised because of an artifact species arising from out-gassing of the KNF Teflon diaphragm pump that partially overlapped

the ethanol elution time and contained the same ion as the ion ($m/e = 31$) used to quantify ethanol. Because of this, ethanol was not included in the TRACE-P data archive. This problem was corrected with the new pump.

The methodology for ozone artifact testing was not straightforward because, as we have empirically discovered, it is difficult to generate ozone without also co-generating carbonyl compounds. Our first approach was to modify the ozone generator (Thermo Environmental Model 565) to minimize the potential for carbonyl artifact generation by simplifying the gas flow path through the system and replacing all standard tubing with inert tubing. Despite these efforts we still found significant artifact formation when generating ozone. We were able to ascertain that artifacts were formed in the ozone generator and not downstream by scrubbing the ozone with granulated KCL after exiting the generator and still observing the carbonyl artifacts; the artifacts were not present when the photolysis lamp was turned off. The solution to this problem was obtained by passing the O_2/O_3 effluent from the ozone generator through a custom designed cryotrap trap filled with glass wool and operated at $-140\text{ }^{\circ}\text{C}$. Under this configuration, the carbonyl artifacts were efficiently trapped while still passing ozone. Ozone concentrations were measured using a Thermo Environmental Model 49.

Figure 11 shows the results of testing our system, as it was configured during TRACE-P, with a number of different ozone levels. The compounds that showed a response were acetaldehyde, propanal, acetone, and butanal. The alcohols and methyl ethyl ketone were not affected by ozone. In processing our data for the TRACE-P archive, the artifact contribution to the signal was removed. The method of standard additions can also be used to remove the artifact contribution to the signal if one assumes that the ambient mixing ratios are not changing over the

calibration period. On an aircraft platform, particularly a rapidly moving one like the NASA DC-8, this assumption is often not valid.

The largest contributor to artifact formation from ozone in our system as deployed during TRACE-P was the rotor material in the VICI valves (Figure 1). The valve rotor material was Valcon E, a polyaryletherketone composite. This material has since been replaced by Valcon R, a Teflon (PTFE) composite that is the most inert material available for VICI valves. There was no evidence of interference or artifact formation from nitrogen dioxide or sulfur dioxide for the FGCMS.

The KNF Teflon diaphragm pump was tested and shown to be an artifact source for acetaldehyde, propanal, butanal, and acetone. Again, no artifacts were observed for methanol, ethanol, or methyl ethyl ketone. As demonstrated in Figure 12, the artifact contribution to the signal increases as the pump rate decreases. This indicates a relatively constant permeation from the pump of these compounds into the ambient air stream being pumped. As indicated earlier, a metal-bellows pump has since replaced this pump. The new pump had not been evaluated fully at the time of manuscript preparation but initial experiments show significantly improved performance.

Results

The FGCMS operated smoothly and was remarkably robust. Data coverage was excellent and the system could operate continuously for more than 15 hours on the initial liquid nitrogen charge. Figure 13 shows a typical example of a chromatogram obtained in flight (TRACE-P Flight 10). Shown are a subset of the compounds that we measured and the ion used for mass spectrometric quantification. Peak integration parameters were optimized for our

chromatographic conditions and the data analysis was automated so that mixing ratios for the target compounds could be ascertained in near-real time and reported to the mission scientist. Before submission to the data archive, however, each chromatogram was carefully reintegrated.

Figure 14 shows results for a subset of our target compounds obtained for Flight 16 originating from Yokota Air Force base targeting the sunrise chemistry of Asian outflow. The top panel shows results for the FGCMS aldehyde measurements along with formaldehyde measurements obtained by Fried et al. [this issue] using a tunable laser diode technique. Superimposed on the data is a trace of the altitude profile. The bottom panel shows results for the FGCMS ketone measurements along with precursor hydrocarbon measurements obtained by Blake et al., this issue. Vertical profiling showed a persistent polluted layer near the surface during this flight and a more polluted layer present at 2-3 km. These data demonstrate the utility of the instrument in observing a number compounds simultaneously and that the instrument response was rapid enough to catch some but not all of the finer structure in the data as the 2-3 km plume was encountered. The data also reveal a shortcoming of the system as configured for TRACE-P. Note the absence of FGCMS data at the highest altitude leg of the flight for aldehydes. At these altitudes, the pumping capacity of our system was insufficient and precluded confidence in these data.

Figure 15 shows a box and whisker plot of the FGCMS dataset collected during TRACE-P. The median value is represented as a solid line. The edges of the box are the 25th and 75th percentiles and the edges of the whisker line represent the 10th and 90th percentiles. Over the entire campaign, median mixing ratios for acetaldehyde, methanol, propanal, acetone, butanal, and MEK were 311, 1085, 136, 808, 63, and 77pptv, respectively.

Conclusions

A GC-MS technique has been developed and deployed for measuring VOC species in-situ on an aircraft platform. The excellent data coverage obtained during this first deployment attests to the robustness of the instrument. Key features of the instrument are that it is sensitive enough to detect low pptv levels of all target analytes and it is extremely selective because target compounds are chromatographically separated and mass selected. Post-mission, the system was fully evaluated in the laboratory and some problems were uncovered with the Teflon diaphragm pump and the rotor material used for the VICI valves. The pump and rotor material have been replaced so that inert surfaces are present throughout the system. The TRACE-P experiment provided an excellent platform for the development and deployment of the FGCMs system and the feasibility of the instrument for in-situ measurements of carbonyl and alcohol species on an aircraft platform has been demonstrated. Substantial additional improvements in the system are clearly achievable. For example, the time response of the system during TRACE-P was 5 minutes. The updated version of the instrument will have a time response of 2.5 minutes. Also, during TRACE-P the number of target compounds was 8; the next version of the instrument will have the capability of measuring over 30 VOCs and CFCs in less than 2.5 minutes.

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Figure Captions

Figure 1. FGCMS inlet and plumbing diagram. See Experiment section B for discussion

Figure 2. Dewar/preconcentration system. The preconcentration system consists of three traps.

Trap 1 is a water removal trap held at $-20\text{ }^{\circ}\text{C}$ during sample load. Trap 2 is the enrichment trap held at $-120\text{ }^{\circ}\text{C}$ during sample load. Trap 3 is the cryofocuser trap held at $-120\text{ }^{\circ}\text{C}$ during transfer from the enrichment trap. Cooling is described in the text. Resistance heating is used for all three traps. Not shown are a heater, used to initially raise the headspace pressure, and a resistor network used to assess the liquid level.

Figure 3. Custom-built gas chromatograph. See text for discussion.

Figure 4. Simplified schema of the zero air generator/calibration system. See text for discussion.

Figure 5. Performance of the zero air/ calibration system (ZA/CS) system. The top panel shows a chromatogram of a standard containing the compounds listed at 3 – 10 ppbv. The bottom panel shows the result of scrubbing the mixture with the ZA/CS at a catalyst temperature of $425\text{ }^{\circ}\text{C}$ and at a flowrate of 5 slpm.

Figure 6. GC-FID chromatogram of permeation tubes (top panel) and high pressure cylinder with concentrations listed in table 2 (bottom panel).

Figure 7. FGCMS graphical user interface.

Figure 8. FGCMS instrument package. The individual components are described in the text.

Figure 9. Laboratory system used for instrument calibration and testing for interferences.

Figure 10. FGCMS calibration curves obtained for target compounds. Each data point represents the average of 5 measurements. The vertical bars represent the standard deviation for the 5 measurements.

Figure 11. Results from interference testing with ozone. Methyl ethyl ketone, methanol, and ethanol showed no response to ozone. Each data point represents the average of 6 measurements obtained on two separate days. The vertical bars indicate the standard deviation of the 6 measurements.

Figure 12. Results of tests showing the artifact produced from the pump used during the TRACE-P experiments. As the pumping rate decreased the relative artifact contribution increased. Methyl ethyl ketone, methanol, and ethanol showed no pump artifacts. Each data point represents the average of 6 measurements obtained on two separate days. The vertical bars indicate the standard deviation of the 6 measurements.

Figure 13. Typical chromatogram, obtained during the TRACE-P mission, of a subset of the targeted compounds. Ions used for quantification for individual compounds are color-coded.

Figure 14. Results from TRACE-P flight 16 for the FGCMS measured carbonyls. The top panel shows the aldehydes measured along with the tunable diode laser measurements of formaldehyde [Fired et al., this issue]. The bottom panel shows the ketones, acetone, and MEK, along with hydrocarbon precursor compounds [Blake et al., this issue].

Figure 15. Box and whisker plot of the species measured by the FGCMS during the entire TRACE-P campaign. See text for discussion.

Table 1. Standard used during TRACE-P (NASA A)

Compound	High Pressure Cylinder gravimetric (ppbv)	% Difference Analysis of mean values*
	Pre-mission values	Post-mission/Pre-mission
Methanol	394 ± 15	-7
Ethanol	48 ± 3	2
Acetone	554 ± 12	-2
MEK	53 ± 3	-2
Acetaldehyde	98 ± 3	-9
Propanal	48 ± 2	2
Butanal	9.6 ± 0.5	-3
Pentanal	25.2 ± 1.5	-34
Pentanone	25.4 ± 1.5	-36
Carbon tetrachloride	4.2 ± 0.1	1

*analysis based on relative calibration factors from FID and represent an average of 3 chromatographic runs.

Table 2. Quantification of standards results

Compound	High Pressure Cylinder gravimetric (ppmv)	High Pressure Cylinder analyzed (ppmv)*	FTIR (ppmv)
Methanol	3.00 ± 0.03	3.0 ± 0.1	2.9 ± 0.2
Ethanol	3.02 ± 0.03	n.d.	2.9 ± 0.3
Acetone	3.03 ± 0.03	3.03 ± 0.08	3.2 ± 0.2
MEK	3.04 ± 0.03	n.d.	2.5 ± 0.3
Acetaldehyde	3.03 ± 0.03	n.d.	3.2 ± 0.4
Propanal	3.03 ± 0.03	n.d.	n.d.
Butanal	3.02 ± 0.03	n.d.	n.d.

*analysis based on calibration factors from permeation tubes
n.d. - not determined

Table 3. FGCMS detection limits during TRACE-P

Compound	Limit of detection (pptv)	Uncertainty (pptv)
Methanol	50	± 85
Acetone	50	± 75
MEK	5	± 8
Acetaldehyde	40	± 60
Propanal	15	± 25
Butanal	5	± 12
Carbon tetrachloride	1	± 0.03

*detection limits determined as 5x the baseline noise. Uncertainty was determined through propagation of errors.

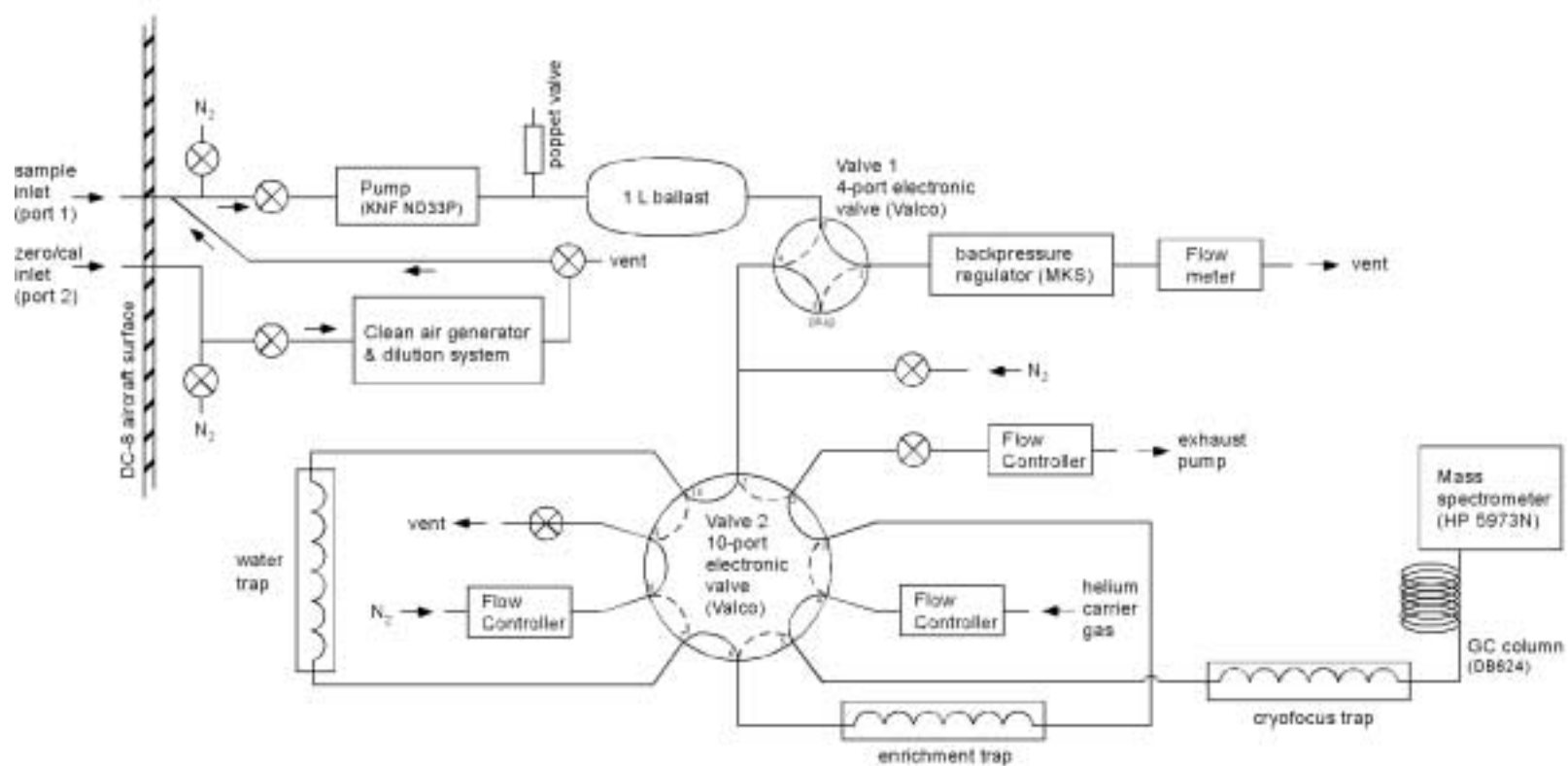


Figure 1

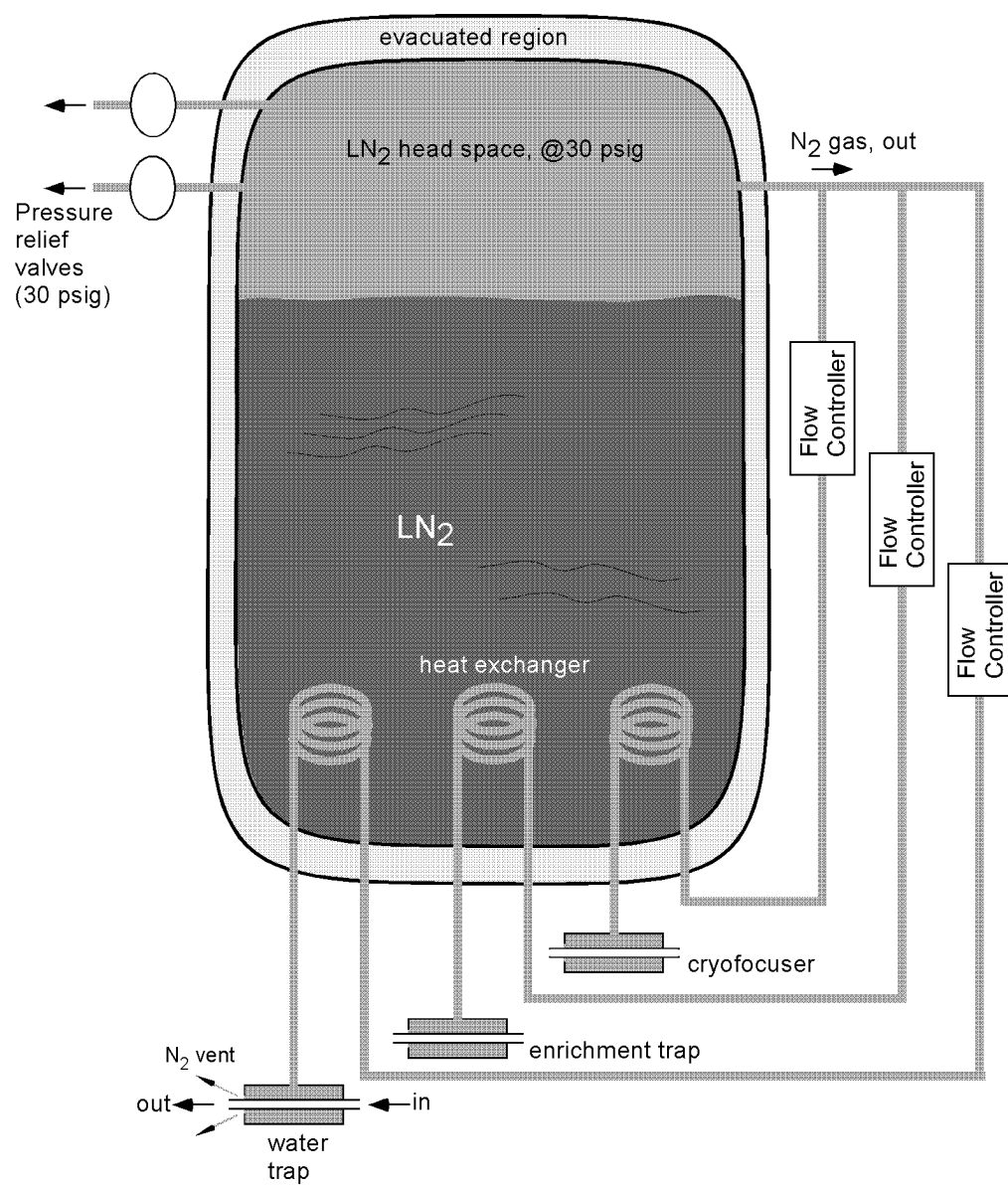


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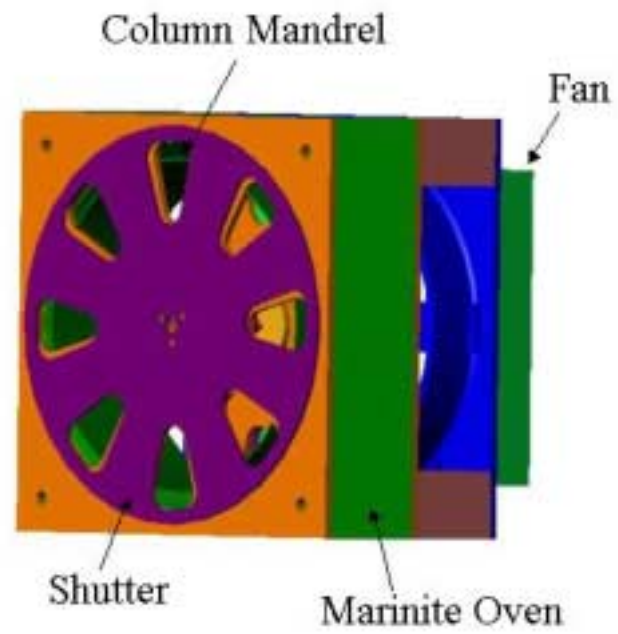


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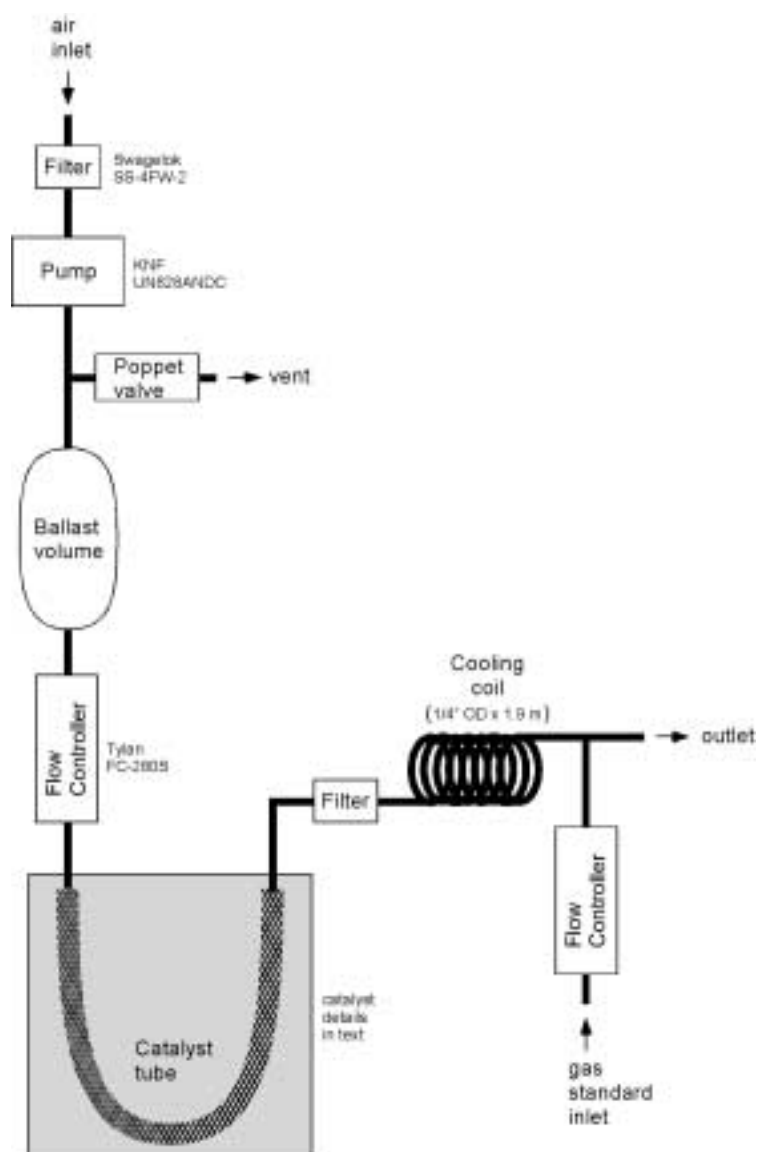


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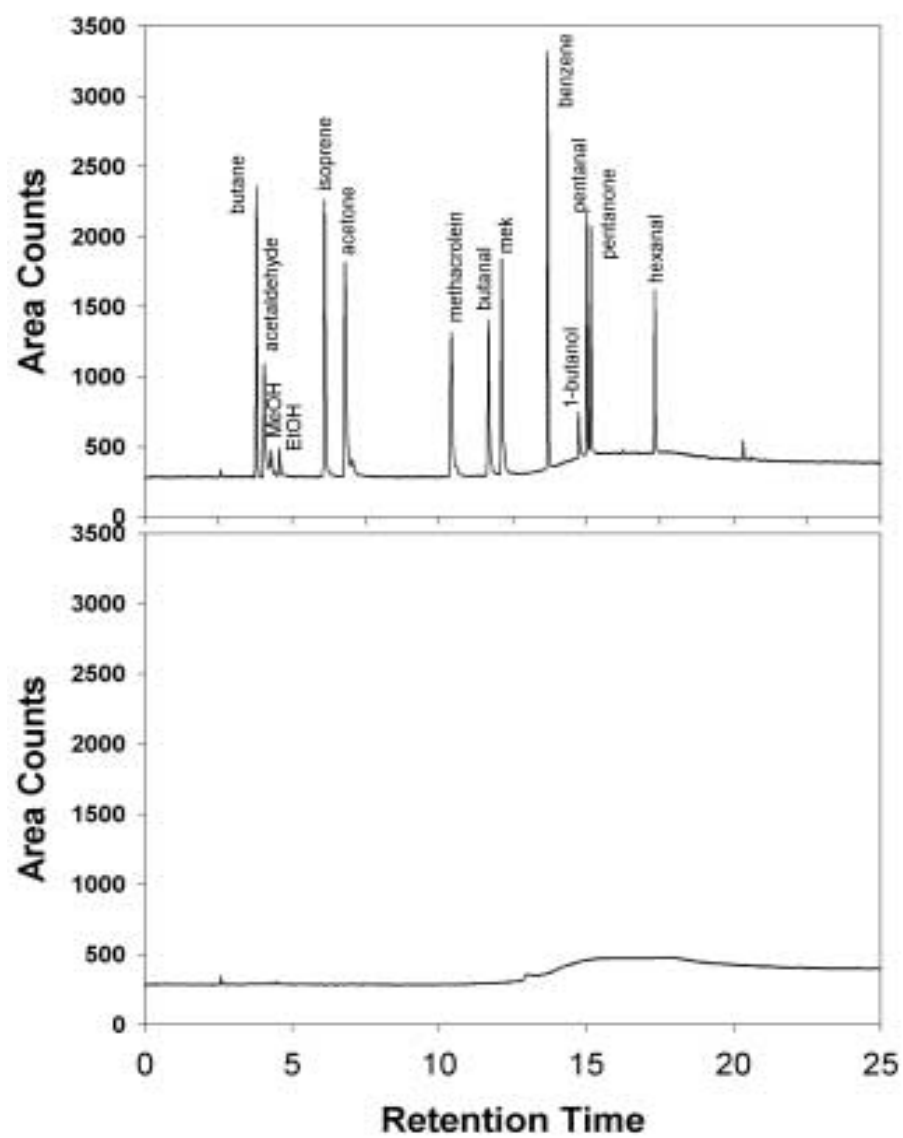


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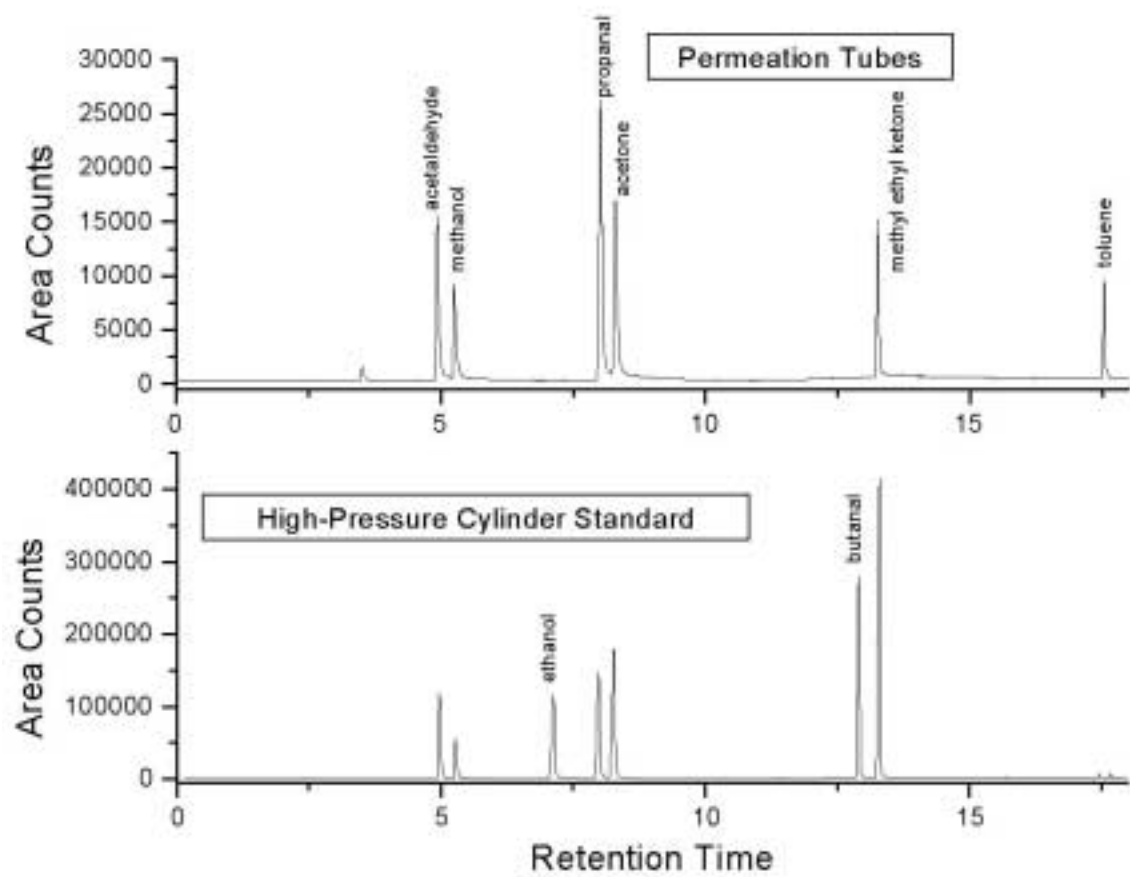


Figure 6



Figure 7

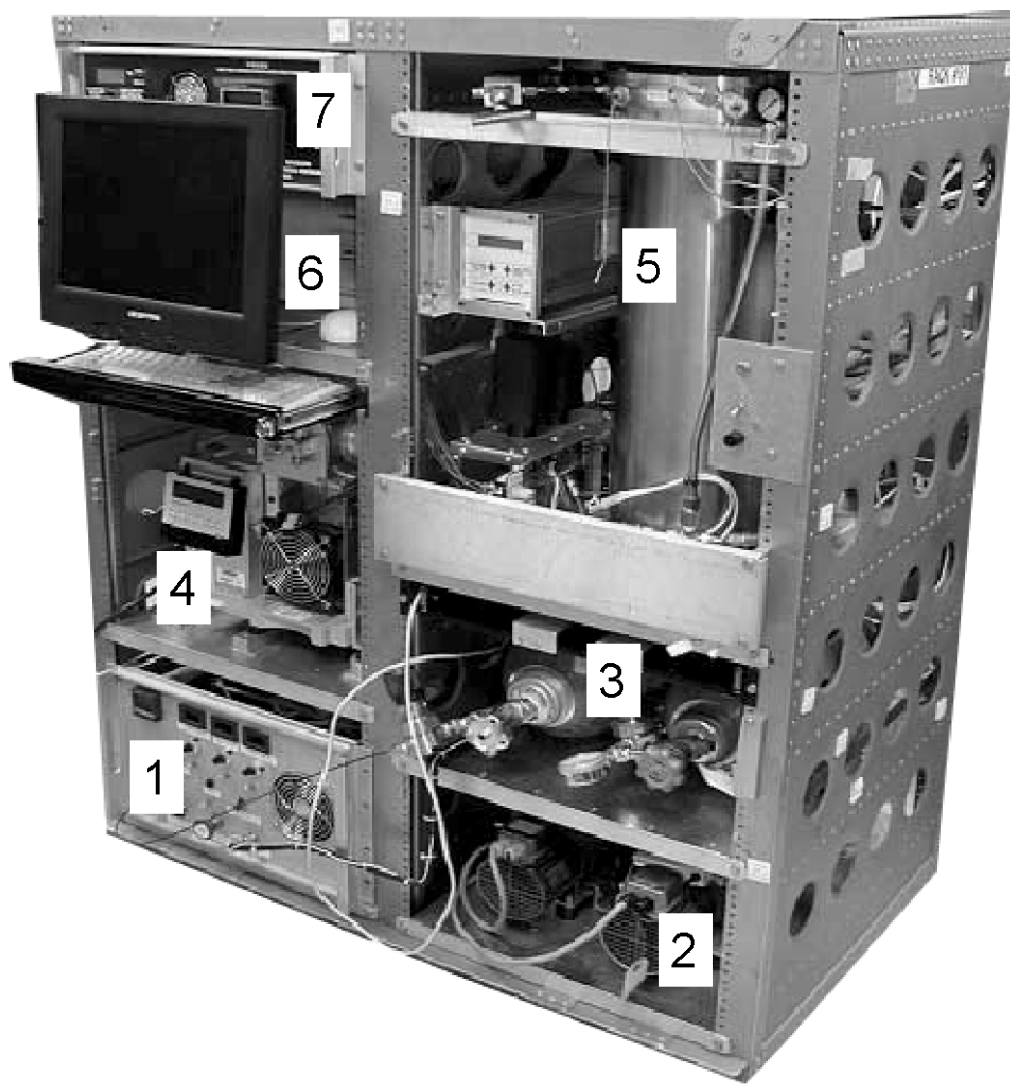


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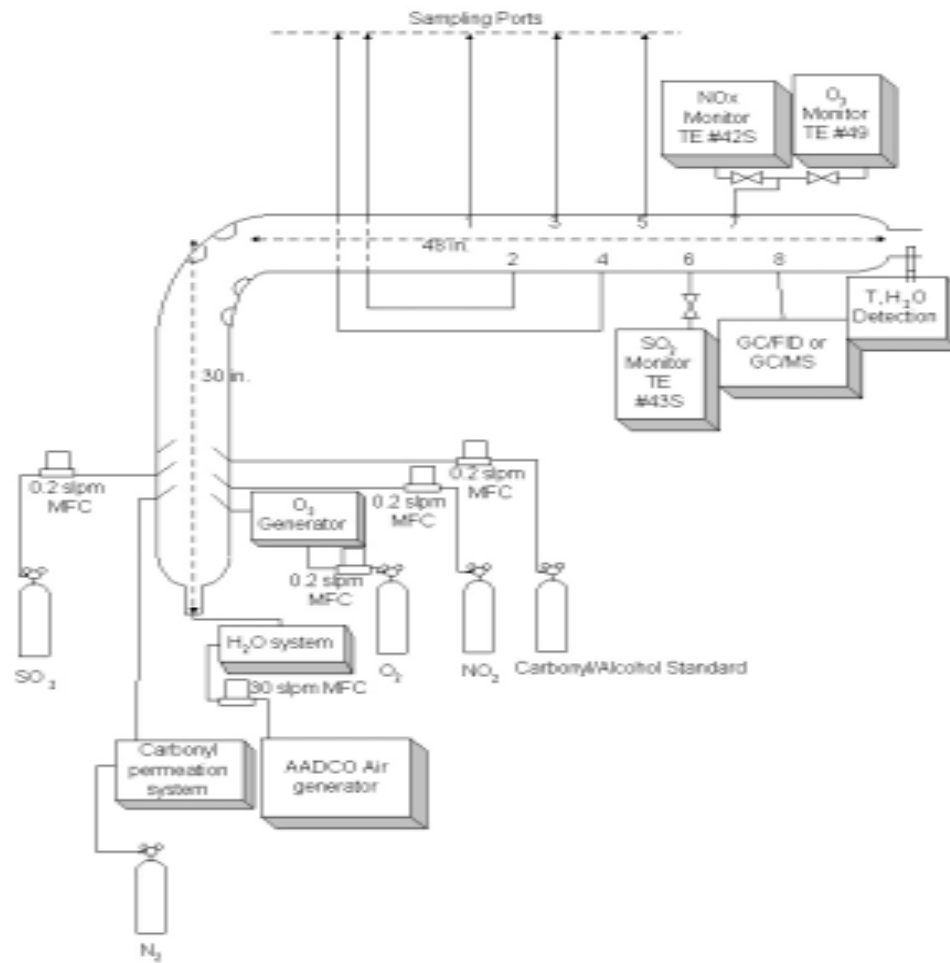


Figure 9

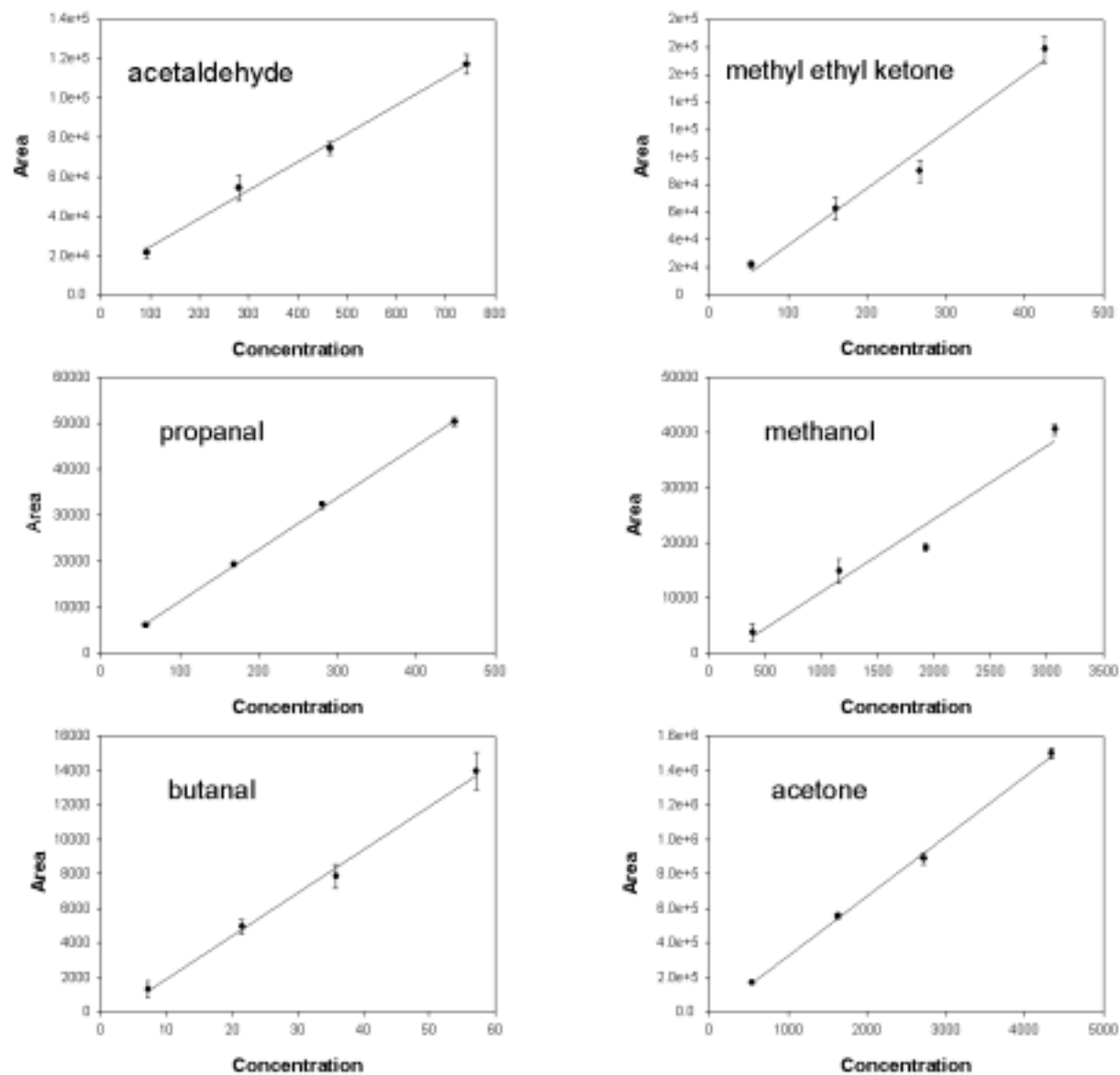


Figure 10

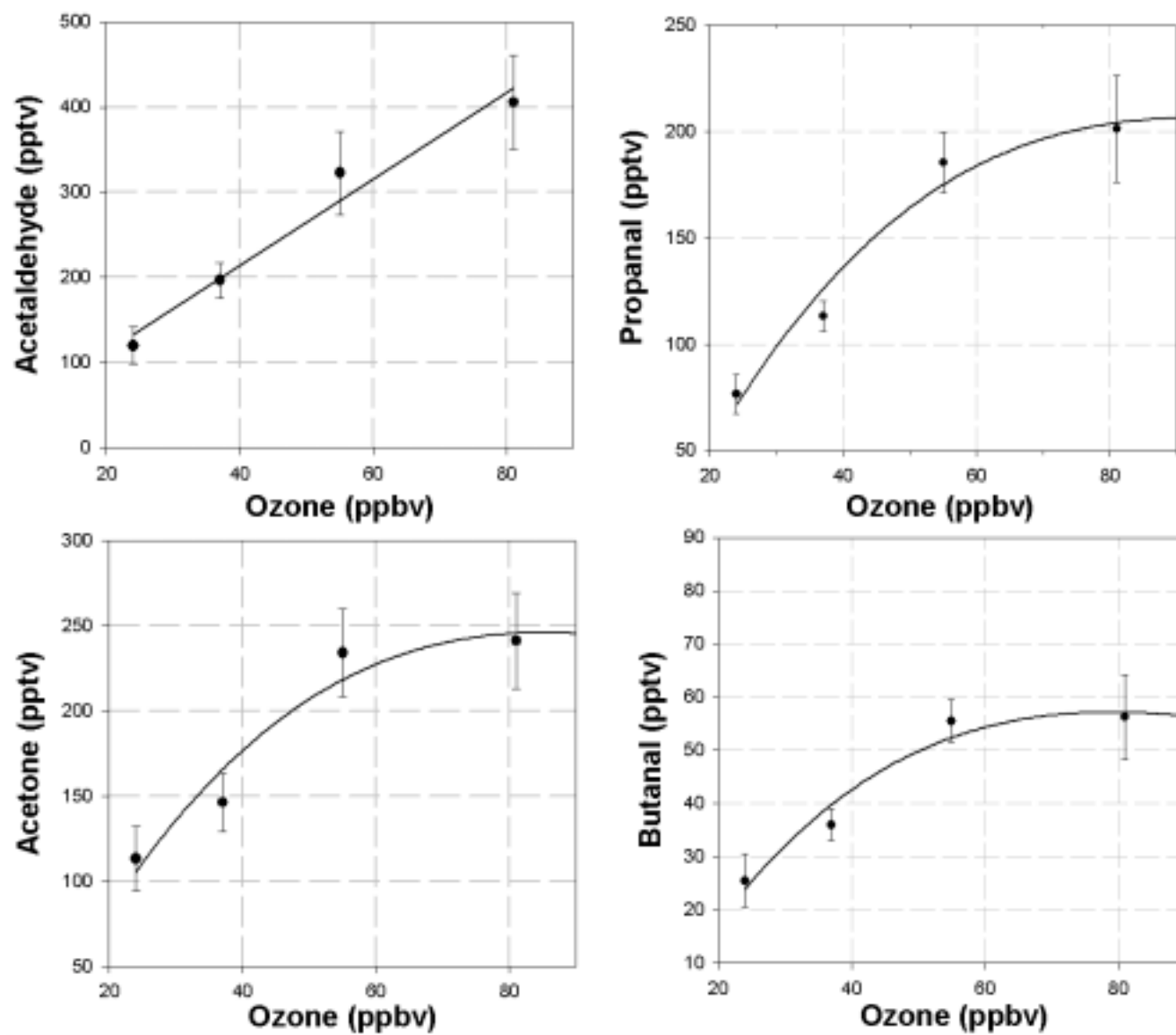


Figure 11

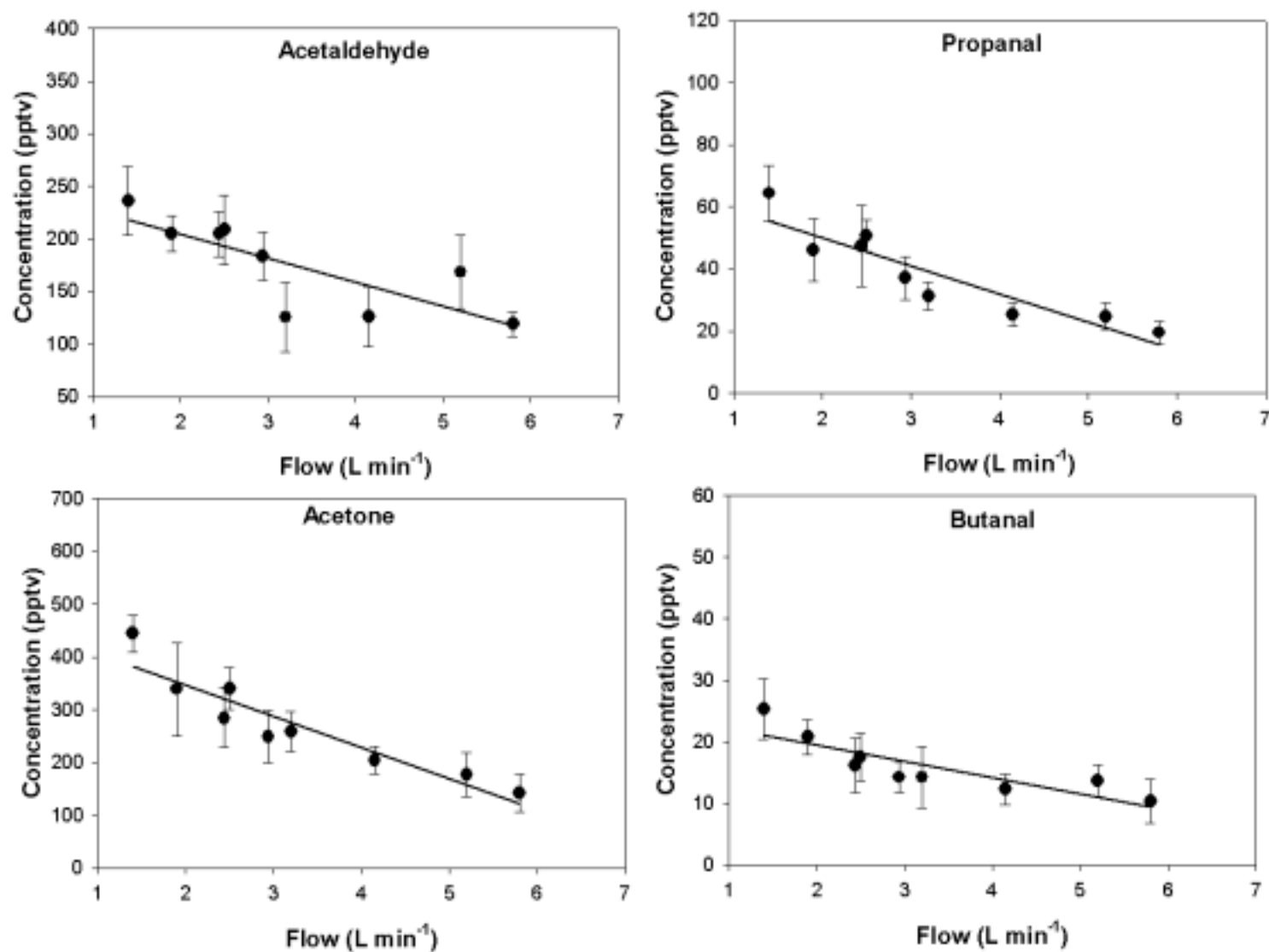
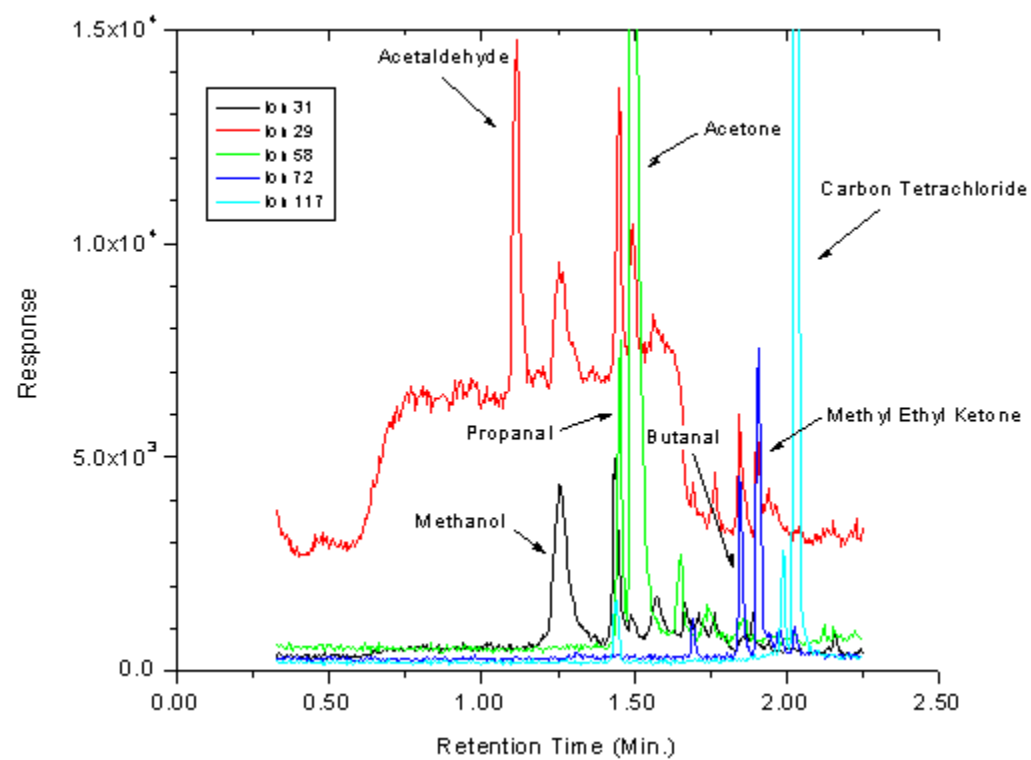


Figure 12

**Figure 13**

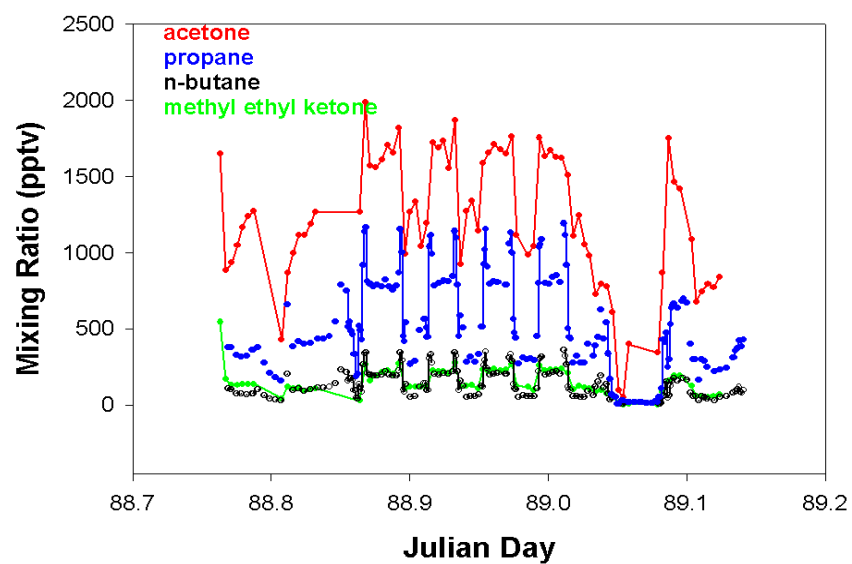
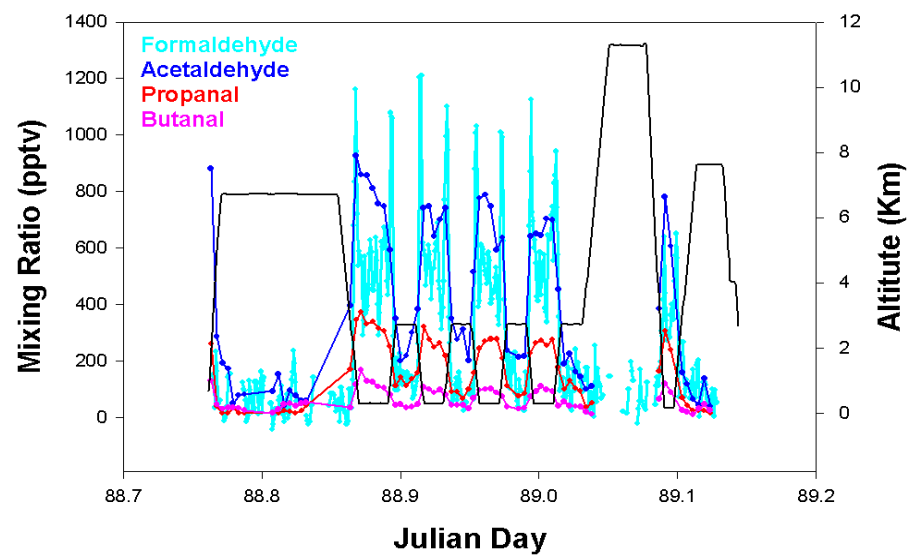


Figure 14

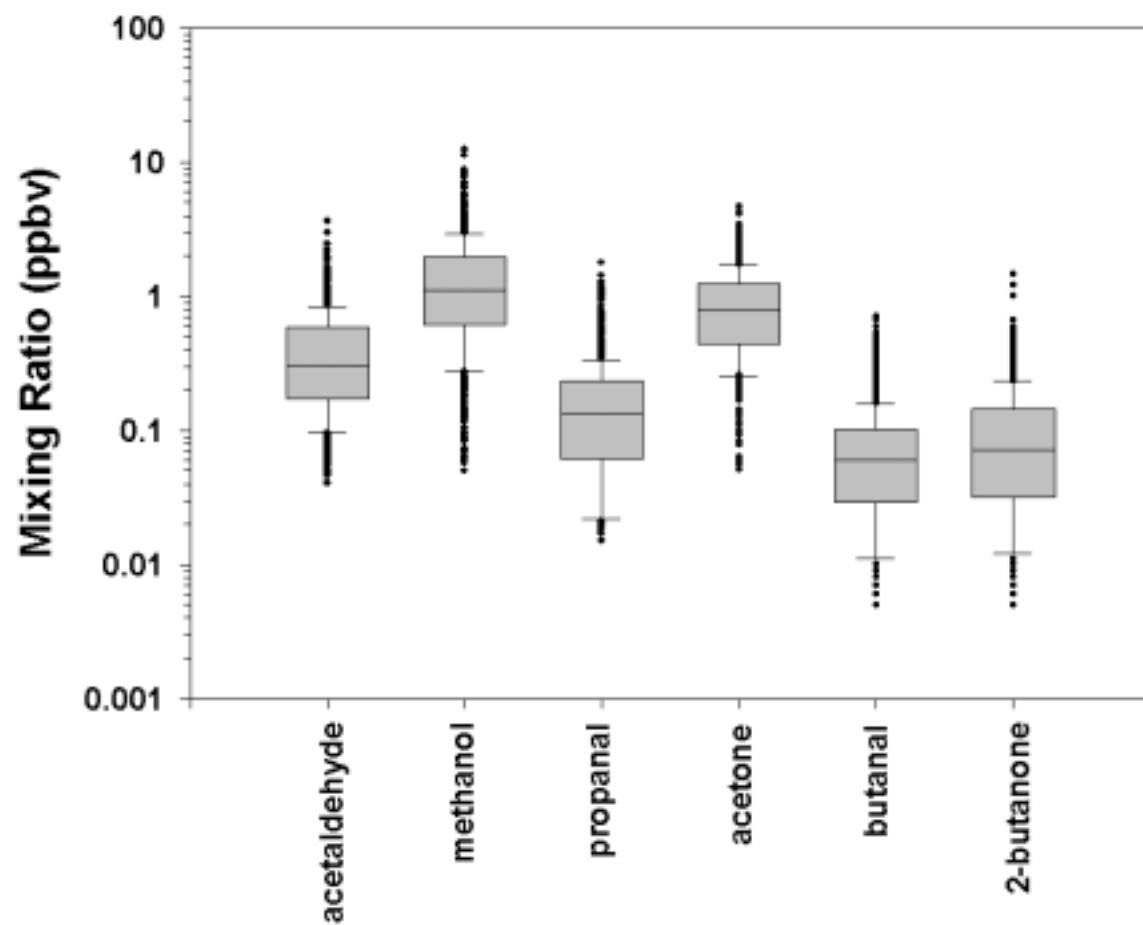


Figure 15.